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# Low Cost Tooling Material and Process for Graphite and Kevlar Composites

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William I. Childs

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# **Low Cost Tooling Material and Process for Graphite and Kevlar Composites**

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## SYMBOLS AND ABBREVIATIONS

Bis A	= Bisphenol A Diglycidyl Ether, Epoxy Resin
CE	= Cyanate Ester Resin
CF	= Carbon Fiber
CTE	= Coefficient of Thermal Expansion
E-SMC	= Epoxy Matrix Sheet Molding Compound
ESTC	= Extruded Sheet Tooling Compound
FS	= Fused Silica, Mineral Filler
SBE	= Synthetic Beta Eucryptite
T <sub>g</sub>	= Glass Transition Temperature of Resin Composition
°C	= Degrees Celsius



Summary: An Extruded Sheet Tooling Compound (ESTC) can be used to prepare a variety of molds and other tools. The ESTC is a very highly mineral-filled, single component, thermoset polymer matrix in the form of a sheet. This sheet is conformed to a pattern, cured to a hard, dimensionally stable form by heating, backed by any number of techniques, and then used as a mold in fabricating composite materials. The primary use is as prototype or short-run tooling.

The primary ESTC composition can be used to produce tooling useful in fabricating composites at temperatures of at least 180°C, and exhibits a low Coefficient of Thermal Expansion (CTE). ESTC tools have been made and used in processes that include compression molding at pressures over 7 MPa, vacuum forming, metal stamping, resin transfer molding, and several low-pressure processes. These tools can be fabricated quickly and at low cost.

Epoxy resins and curing agents are the primary matrix materials studied. The matrix must be a low viscosity liquid to allow incorporation of a high concentration (80%) of inorganic mineral filler. The system should cure to a dimensionally stable condition in a few hours at temperatures less than 90°C to allow use with typical pattern materials. Final cured properties of the ESTC include dimensional stability and chemical resistance and strength at temperatures of 150-180°C used in fabricating high performance composites. A very low CTE, close to that of carbon fiber composites, is also desired.

Two compositions were developed as ESTC materials plus a manufacturing process and application techniques. One composition, based on a combination of cyanate ester and epoxy resins, provides glass transition temperatures over 180°C and good strength at that temperature. The second composition, based on an epoxy/amine matrix, is designed for general use at temperatures of 150-160°C. A variety of tools were made using these ESTC materials, and composite parts fabricated from these tools.

INTRODUCTION: "Soft" or "plastic" tools have assumed a major role in the fabrication of components and structures made from composite materials. Compared with permanent, usually metal, tools, these soft tools are lower in cost, lighter in weight, and much faster to construct. A typical construction begins with a thin (1-2 mm) gel coat containing a high resin content that is applied to a prepared pattern. This is followed by multiple layers of thermosetting resin and reinforcing fabric until a thickness of 6-15mm is achieved. After this shell is cured, it is backed using one of a variety of techniques to confer strength and stiffness and provide a supporting structure. Tools built in this manner work well in many situations, but they are subject to several drawbacks. It is difficult to ensure that air is not entrapped during the build-up of the many layers of resin and fabric; the surface gel coat is resin-rich and consequently has a high coefficient of thermal expansion (CTE); the usable temperature range for these systems is typically limited to about 125°C; and the thermal expansion of the completed tool is several orders of magnitude higher than that of most advanced composite materials so that dimensional accuracy of the furnished part is difficult to achieve.

Phase I study<sup>1</sup> demonstrated that a new concept in making plastic tools offers the opportunity to reduce or eliminate many of these problems associated with current plastic tooling. A single component formable sheet can be used to prepare the actual tool surface. This extruded sheet tooling compound (ESTC) can possess a number of desirable characteristics for use in fabricating components from advanced composite materials. These include:

- . Unusually low CTE
- . Usable at temperatures of at least 175°C
- . Not subject to problems of delamination and surface spalling
- . Excellent chemical resistance
- . Very low shrinkage on cure

The initial work on this project<sup>1</sup> demonstrated that a sheet material could be made using epoxy compositions similar to those used in many high performance composites. These compositions can be filled to about 80 percent (weight) with particulate minerals possessing low CTE; mixed; and then formed into a sheet 6mm thick. This sheet was shaped to a pattern and heat cured to a dimensionally stable form. Sample parts were then fabricated using this cured ESTC as a mold.

This report describes the continuation of that work. The primary objectives were to develop an ESTC that: Would have reproducible properties of low CTE and usefulness at temperatures of 175°C required for curing many current advanced composite materials; be fabricated into tools by individuals after minimal training; and that can be manufactured in a reproducible manner. The work involved formulation studies, development of techniques of use, development of a manufacturing process, and user evaluations.

Techniques for making a tool using ESTC will be described along with some of the initial use applications. This will be followed by discussion of the compositional and manufacturing process studies.

#### 1.0 ESTC Requirements

The characteristics required for formulating an ESTC and the procedures that have been developed for making a useful tool from that ESTC are basically the same no matter what the composition:

<sup>1</sup>Phase I NASA Contract

- . Ability to form a sheet that can be physically handled.
- . Will accept a high concentration of mineral filler in order to achieve lowest possible CTE.
- . Sufficient material flow to conform to the pattern while retaining the basic sheet character.
- . Maintain physical strength, dimensional stability, and chemical resistance at temperatures at which it will be used in fabricating composites.
- . Sufficient shelf life and working time to be usable in an industrial environment combined with relatively fast cure cycles.

Many of these characteristics conflict so that the proper balance must be established to provide a practical and usable ESTC.

## 2.0 Use Procedure

The procedure that has evolved for preparing a tool using ESTC is outlined below. The techniques and equipment required are widely used in the aerospace industry, but not as widely used in, for example, the automotive industry.

1. Preparation of the pattern -- Typical pattern materials such as wood, plaster, and metal or plastic parts, can be used with ESTC. Normal procedure is to seal the pattern and then apply a release coat. The best release is a sprayed coating of polyvinyl alcohol (PVA) for use on almost any pattern material. Over 40 release agents/systems were evaluated with ESTC on metal, glass, wood, and plastic surfaces. Some worked well on a particular substrate, but not on others. PVA could be used with any substrate and was used in most experiments.
2. Application of the ESTC -- The ESTC is allowed to warm to room temperature and then the surface is dusted with a layer of glass spheres (smaller than 200 mesh). The most difficult problem in achieving a void-free surface when using ESTC is to completely remove the small quantities of air that are trapped between the sheet and the pattern. Carefully applying and rolling the sheet by hand does not eliminate this air. The use of vacuum is the only way to accomplish this consistently. The effectiveness of the use of vacuum was controlled by the relative stiffness and tackiness of the sheet. If the sheet is too soft, it deforms readily during application and traps small air pockets on the pattern. If it is too stiff, the sheet may crack when it is being conformed to the mold. The ideal sheet for handling has the consistency of stiff bubblegum and a dry surface. By dusting the ESTC surface with fine glass beads, the effectiveness of the vacuum was increased dramatically. The beads will then be wet by resin during the remainder of the cycle.

Multiple sheets of ESTC are required for forming large tools. Joints between sheets can be formed using either lap or butt design. There is sufficient flow of the ESTC to fill in joints as long as the gap is 2mm or less.

In some designs featuring deep draws or sharp angles, it is desirable to fill in with extra pieces of ESTC. With some of these contours, the vacuum bag will bridge and a way must be found to maintain pressurized contact with the ESTC and pattern. For some deeper draws, ESTC must be added to ensure that excessive thinning of the main sheet does not occur.

In some pattern areas where it may be difficult to remove trapped air, it is helpful to perforate the ESTC with holes up to 1.0mm in diameter. These perforations will heal during the rest of the process.

3. Vacuum Bag -- Following application of the ESTC to the pattern, the assembly is then enclosed in a vacuum bag. Conventional techniques are used and the bag material can be nylon or silicone rubber. Four-mil polyethylene film works especially well because its flexibility provides better surface conformance and high temperature resistance is not needed. Vacuum is then applied. A recommended minimum of 500mm Hg vacuum is desired.
4. Initial Cure -- The assembly is then placed in an oven while the vacuum is maintained. Oven temperatures of 65-90°C can be used. Minimum cure time varies depending on the specific ESTC formulation and the temperature. Typically, this can range from 12 hours at 65°C to 4 hours at 90°C. In most of the work, it has been convenient to use a temperature of 75°C and allow the ESTC to cure overnight on the pattern.
5. Backing -- The appropriate backing is then placed on the formed ESTC. This can be done while the ESTC is still on the pattern or after it is removed. At this time, any repair required can be done. If small air voids occur, they can be fixed by hand using bits of ESTC.
6. Final Cure -- A final postcure is then given for 2-4 hours. The curing temperature is dependent upon the particular formulation and is typically the final use temperature for that formulation. The tool is then ready for use. No measurable dimensional change occurs during this final cure and the pattern will fit exactly into the finished tool.

### 3.0 Tool Building

During the program, a number of tools were built and several were later used to fabricate parts, both in-house and at outside facilities. The objective of the earliest work was to gain experience in using ESTC and in finding potential problems with its use. The primary pattern used in this early work was for part of a motorcycle housing measuring approximately 45cm by 20cm with a curved surface and a 90 degree corner. This proved to be a good experimental pattern since the corner had a pronounced tendency to trap air. An ESTC tool from this pattern is shown in Figure 1. Many of the basic handling techniques for ESTC were developed using this pattern. Other tools that were made during this program, primarily for internal use, included:

- a) Cylinder head for compressor -- This part has relatively deep ribs and bosses. Several compression molds were built using different backings and mold construction. These were used to compression mold high glass content epoxy composites (ESMC) at conditions of 150°C and 7-12 MPa molding pressure.
- b) Hinge for rear van door -- A compression mold was made for this hinge. Parts of high glass content ESMC were molded in this ESTC tool, and were compared to parts molded in a steel mold and found to be equivalent.
- c) Flexural test specimens -- An ESTC mold for 2.54cm by 10.1cm by 0.31cm bars was made and then used to make test coupons from ESTC materials.
- d) An ESTC mold is being used in the formulation and testing of a special epoxy prepreg being developed for a composite airframe program with an aerospace company in Missouri.

A number of evaluation studies of ESTC were made in conjunction with specific programs for potential users. Several of these evaluations involved on-site work at the customer facility, while others were done primarily in-house. These studies are summarized below and include a discussion of ESTC problems that occurred during each evaluation:

- a) Mold for vacuum forming -- The tool was made to meet a 3-day deadline. It required only one finished surface and was similar in shape and slightly larger than a household double kitchen sink. The tool was constructed as described earlier and backed with several layers of glass cloth and epoxy. Several voids 6mm in diameter or smaller required patching prior to final cure. The user reported experiencing no problems with the tool over a period of almost one year. Use temperature was 125°C maximum.
- b) Compression mold for bracket -- This was the first compression mold made with ESTC. The bracket is roughly triangular in shape and 16cm high, 10cm at the base, and 1cm thick. The ESTC was backed by casting a highly filled epoxy against the ESTC. Brackets were compression molded of E-SMC at 140-150°C and 5.5MPa. Cracks occurred at several points. These cracks were caused by tensile stresses placed on the ESTC during compression molding of the E-SMC. Another ESTC tool was built and backed with 5mm of fiberglass cloth/epoxy followed by the epoxy casting. Molding of the E-SMC was repeated. Two small cracks occurred, but became filled with compound and did not interfere with molding. Over 40 brackets were molded from this tool with very little change in the ESTC after the first few shots. The use of fiberglass cloth/epoxy laminated to the back of ESTC became a standard practice for future ESTC tools.
- c) Mold for resin transfer -- A tool for resin transfer molding a segment of an outboard motor housing measuring approximately 43cm by 33cm was fabricated in collaboration with a major molder. Each half of the two-part mold measured approximately 95cm by 75cm by 40cm deep and was built inside a steel frame and cored for steam heating. Fabrication of the ESTC surface for the female mold half was first attempted at an outside facility having an autoclave. The resulting surface had excessive voids and was not satisfactory. Preparation of the female was repeated in-house and a satisfactory surface achieved. Placement of heating coils and mold backing was completed by the molder. The female mold half was then tested by steam heating. The mold cracked at a temperature of about 65°C and the crack opened further as heating continued. It was determined that the cracking had been caused by thermal expansion pressures of the commercial epoxy mass-cast system used as backing for the tool. The CTE of the backing was found to be 3 to 4 times larger than the CTE of the ESTC.

This problem emphasized the importance of matching the thermal expansion of the backing material closely to that of the ESTC. A study was begun to look at available backing systems for use with ESTC. Most of the polymer based systems exhibit this higher CTE and so the search for better backings continued throughout the program. A simple backing was found that resolved the immediate CTE mismatch problem. A mixture of coarse sand (80 percent) and the resin and curing agent of the ESTC (20 percent) was made and cast behind the ESTC/fiberglass surface. This sand/resin backing system is usable for most low pressure tools.

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Figure 1. Motorcycle Housing -- This pattern (light color) used for much of the early testing.  
ESTC tool taken from this pattern.

The ESTC for the male half was formed using the female mold plus sheet wax. The resulting ESTC surface had no flaws, and the mold was completed using sand/resin backing. The completed mold was then used to mold parts of polyester-fiberglass using three different processes: Compression molding with SMC, liquid resin molding, and resin transfer molding. Molding temperatures ranged up to 135°C. The part molded in this tool is shown in Figure 2.

- d) Transmission housing mold -- A pattern was received for a vehicle transmission housing (half). Several ESTC surfaces were made. The pattern contained areas having vertical sections over 5cm high and several recesses. A good surface was not achieved because the geometry of the part did not allow complete air removal, and the vacuum bag bridged over recessed areas, resulting in poor reproduction. An attempt was made to see if the resulting tool could be nickel plated, but adhesion of nickel to the ESTC was not acceptable.
- e) Stamping die -- A tool was made at an aerospace company in Texas for use as a die for stamping aluminum. These parts are replacement panels for the Cobra helicopter and are approximately 125cm by 75cm. There were a few small cracks in the ESTC surface, which were due to the technique used in making the tool and can be readily corrected; the tool produced satisfactory stamped parts.
- f) Compression mold for cup -- A cup pattern similar in shape to a typical plastic coffee cup was used in an attempt to make a compression mold. A variety of ESTC placement and vacuuming techniques were tried, but a void-free surface along the walls was not achieved. Apparently the ESTC around the edges consistently seals tight before air can be completely removed by the vacuum.
- g) Fan shroud mold -- A single side mold was made for a fan shroud, shown in Figure 3. Dimensions are 40cm by 40cm. The mold is to be used for lay-up of polyester fiberglass. Before being put into use, the design was changed and a new ESTC mold will be made when the new design is ready.
- h) Compression molds for automobile convertible top rails -- Compression molds were made for both right-hand and left-hand rails. These parts are shown in Figure 1 and the procedure used is illustrated in Figures 4 through 11. Aluminum parts were used as the patterns and ESTC surfaces were then backed with fiberglass epoxy laminate followed by a filled epoxy backing. After completion, the molds were used to make 10 to 12 parts each from E-SMC. Some chipping of ESTC occurred on sharp edges that were used as shear edges in the mold. Sections of ESTC thinner than 0.5cm are not strong enough to be used alone in high pressure molding. It will be necessary in such situations to design the mold to eliminate these thin sections.
- i) Other tools -- An aerospace company in Connecticut made a prototype mold of ESTC and used it to successfully mold a component from polyphenylene sulfide engineering thermoplastic. Another company in Washington made a mold for fabricating buggy seats of polyester fiber glass (Figure 12). An aerospace company in Georgia has received ESTC for evaluation as tool building material. Another aerospace company in Texas has specified use of ESTC in a proposal they have submitted. It will be early 1987 before the ESTC will be used, if the bid is successful.

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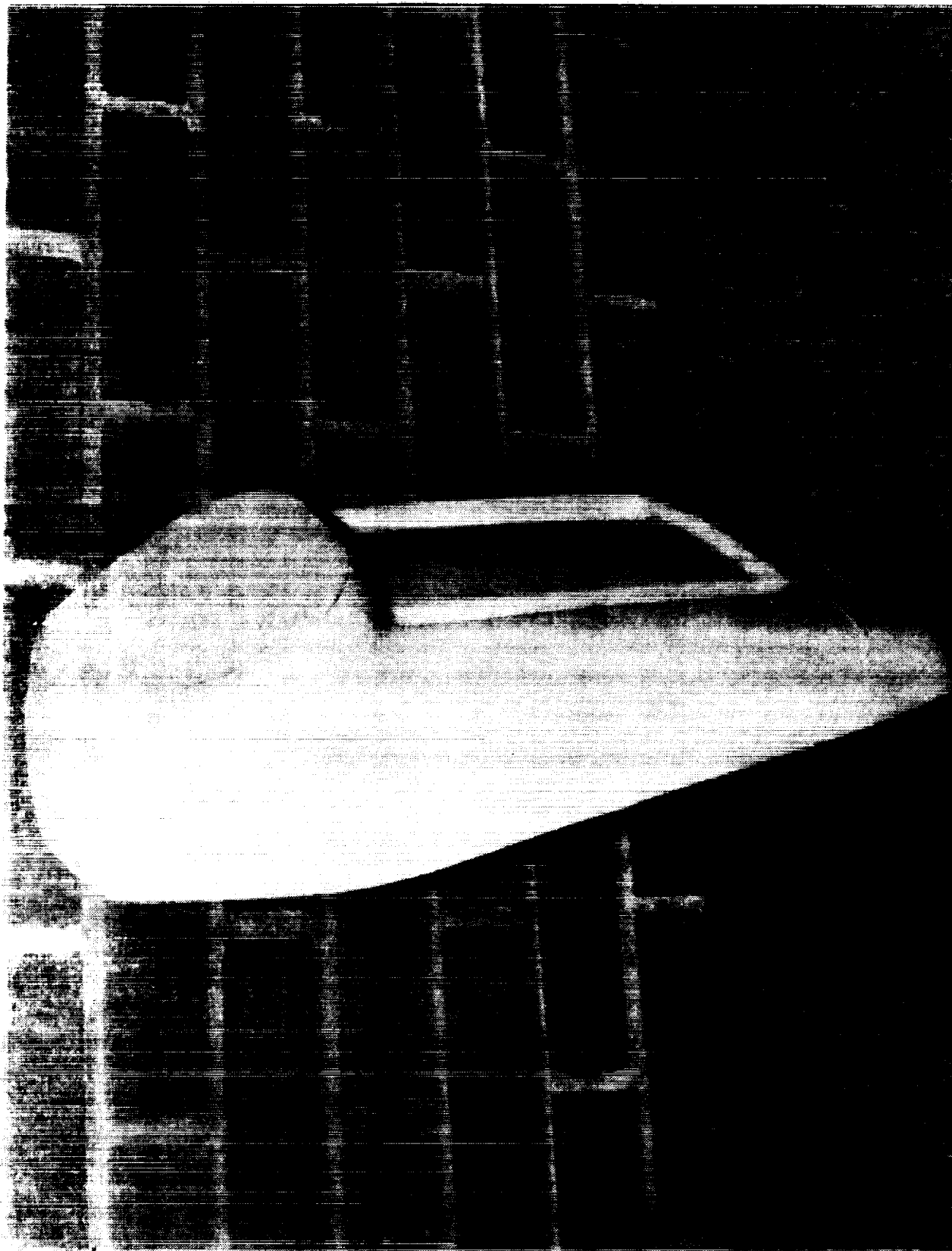


Figure 2. Outboard Motor Housing -- ESTC mold was used to fabricate this part by resin transfer molding.



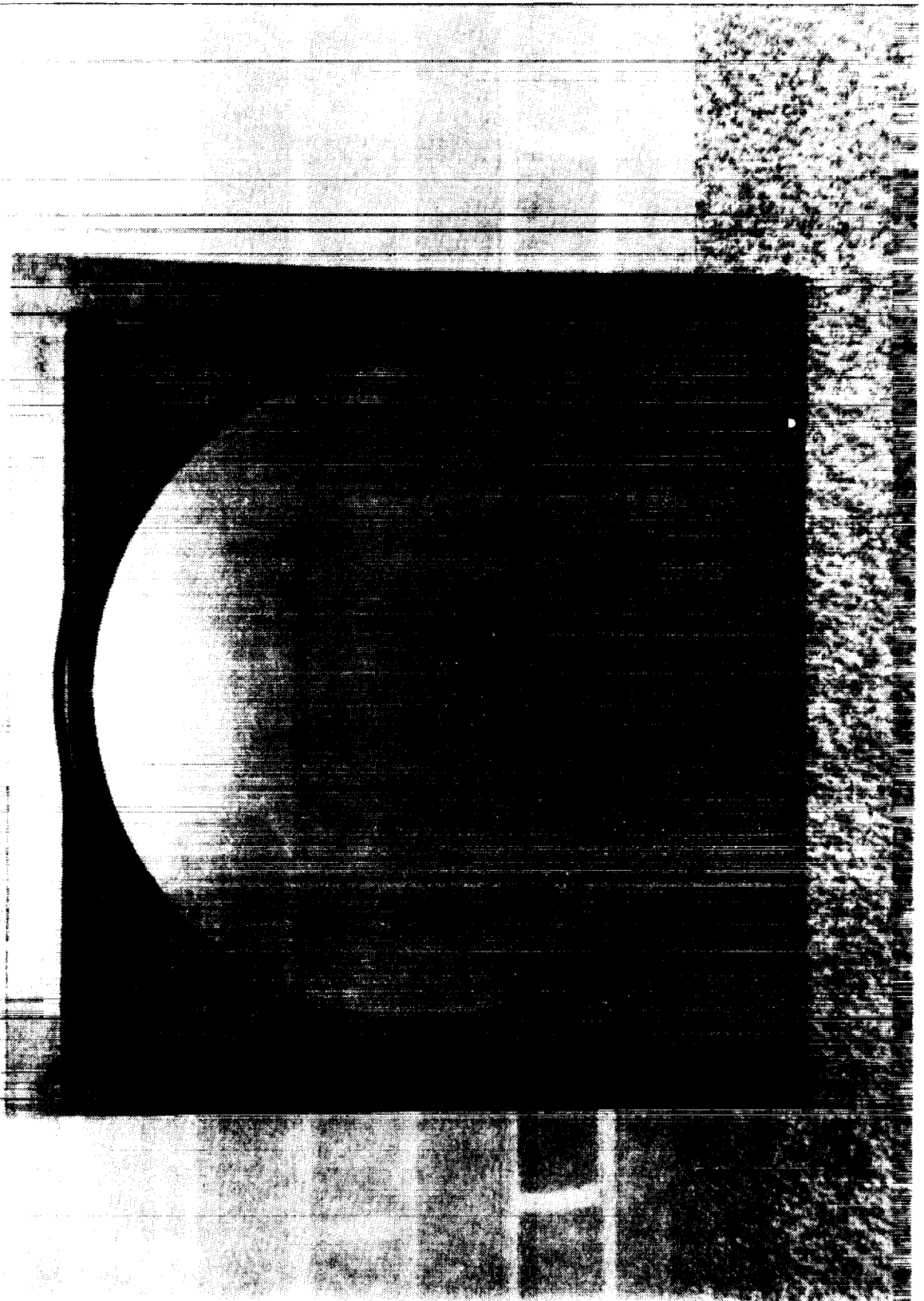


Figure 3. Fan Shroud Mold of ESTC.



Figure 4. ESTC -- Sheet of ESTC showing room temperature pliability.

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Figure 7. Perforating ESTC --- Holes can be made in ESTC to assist escape of air.

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Figure 8. Placement of ESTC -- Sheets of ESTC are placed on the pattern to approximate shape.

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Figure 9. ESTC in Place -- Butt joints between pieces of ESTC.



Figure 10. Vacuum-Bagged Assembly --- ESTC sheet and pattern in vacuum bag.

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Figure 11. Mold and Components -- Two halves of finished ESTC mold; part molded of E-SMC (foreground); and pattern (white) used in making the mold halves.



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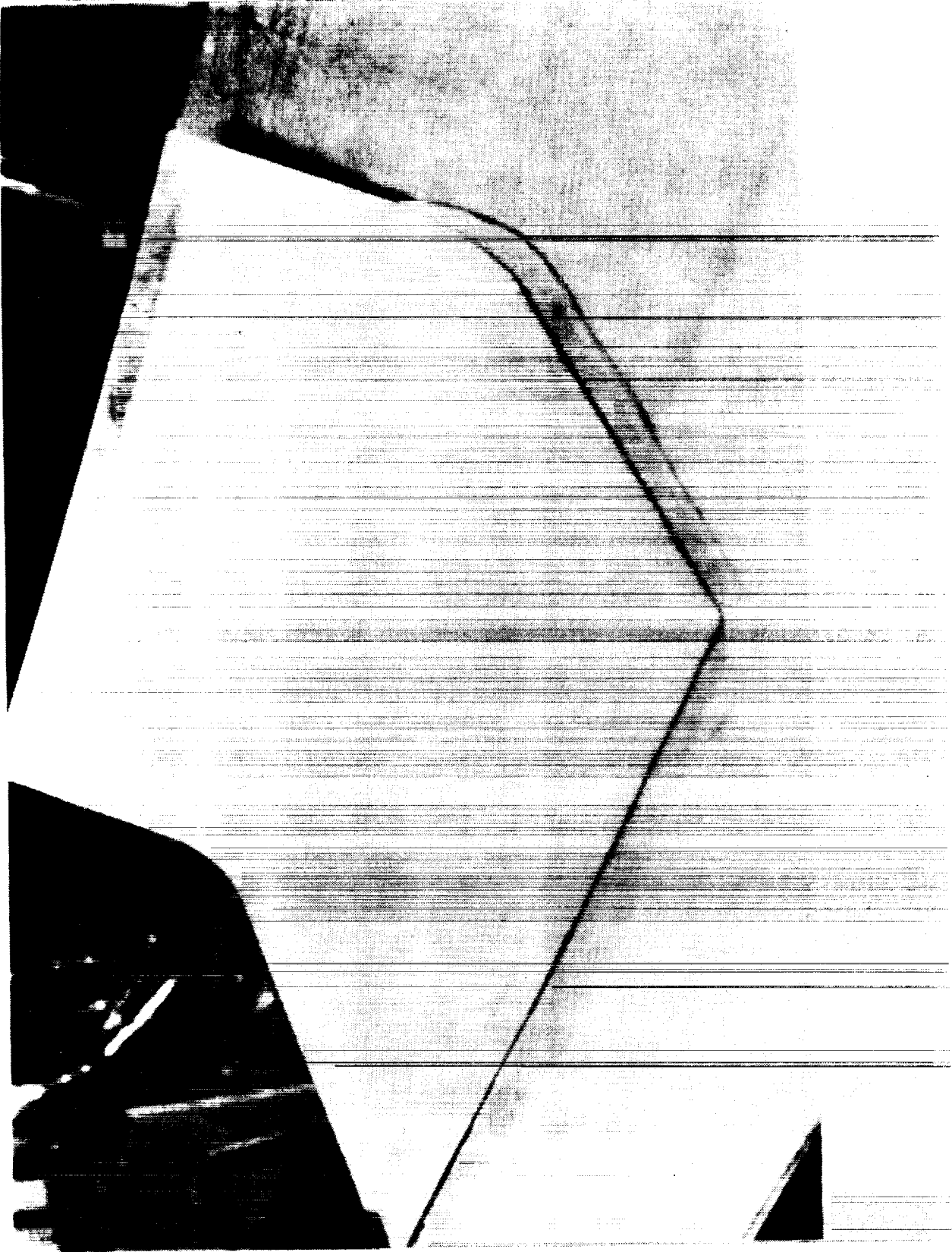


Figure 12. Buggy Seat -- Made using ESIC mold.



#### 4.0 ESTC Variation

The experience gained from building these experimental tools with ESTC has demonstrated that tools for use in a variety of composite fabrication processes can be fabricated quickly from ESTC. During the course of the program, a number of problems were encountered that led to changes in the composition of the ESTC. These are discussed below along with the discussion of the research done to develop the 4 types of ESTC proposed in Phase I.

Type 1. Use at 175°C and very low CTE.

Type 2. General use up to 150°C where CTE is not as critical.

Type 3. Thin sheet (2-3mm) ESTC.

Type 4. Room temperature curable ESTC.

All of these require different chemistry and/or filler, but the basic manufacturing process and use procedures are essentially the same.

The main thrust of the program is to develop a Type 1 ESTC that can be used to make tools for fabricating high performance composites. This requires that the ESTC be usable with composites containing carbon and aramid fibers and that are cured at 175°C. To have usefulness at 175°C, the ESTC needs to have strength and chemical resistance at that temperature and our goal was to achieve a Tg minimum of 175°C. For use with carbon and aramid fiber composites, the goal was to reduce the CTE as close as possible to  $3-5 \times 10^{-6} \text{ cm/cm/}^\circ\text{C}$ .

The ESTC formulation developed in Phase I is shown in Table I. The chemistry is related to that of the most widely used epoxy matrix for high performance composites. It possesses many of the properties desired for an ESTC, but further work showed that it was not satisfactory in several aspects. The required cure is too long and too complex. Catalyzing for faster cure did not provide significant improvement. The ESTC did not hold well on vertical surfaces or corners, resulting in uneven cured thickness. Of critical importance, the high temperature required to mix and process the formulation allowed a temperature window of only about 10°C and larger batches could not be made reproducibly. During several attempts to make larger batches, the reaction became uncontrollable.

Most of the compositions studied for use in ESTC were based on epoxy resins because of their overall properties and handling characteristics. Usable epoxy resins were limited to those having low viscosity so that high filler loadings could be achieved while the compositions were mixed at temperatures below 90°C. A list of types of epoxy resins that were studied is shown in Table II. Most epoxy resins designed for high temperature use have high viscosity and, therefore, required higher mixing temperatures or the use of diluents to achieve satisfactory mixing at high filler levels. It was found that a conventional Bisphenol A based liquid epoxy resin has the best overall combination of properties for most ESTC formulations, plus the lowest cost.

Many types of curing agents were evaluated with Bis A and other epoxy resins (Table III). Attempts to use solid, latent curing agents such as dicyandiamide were unsuccessful since the resin appears to wick away from the curing agent during vacuum bag cure, resulting in a sticky surface. Liquid anhydrides can be used and offer the advantage of relatively longer shelf life. This longer shelf life is achieved at the sacrifice of longer cure times. Aliphatic and similar fast curing amines do not offer enough working time to prepare and use an ESTC.

TABLE I

Initial ESTC Formulation

Tetraglycidyl Ether of MDA . . . . .	5.1%
Alicyclic Diepoxy Carboxylate. . . . .	5.0
Diglycidyl Ether of BisA . . . . .	0.6
Diamino Diphenyl Sulfone . . . . .	5.8
Schott Glass . . . . .	79.7
Potassium Titanate Whiskers. . . . .	2.9
Sub-Micron Silica. . . . .	0.4
Epoxy Silane . . . . .	0.5
	<u>100.0%</u>

TABLE II

Epoxy Resins Evaluated in ESTC Formulations

Diglycidyl Ether of Bisphenol A  
 Diglycidyl Ether of Bisphenol F  
 Diglycidyl Ether of CHDM  
 Tetraglycidyl Ether of MDA  
 Tetraglycidyl Ether of MXDA  
 Epoxidized Phenol Novolac  
 Epoxidized Cresol Novolac  
 Glycidyl Ether of Trisphenol  
 Alicyclic Diepoxy Carboxylate  
 Diglycidyl Ester of Phthalic Acid  
 Polyglycidyl Ether of Polyhydric Alcohol

TABLE III

Types of Curing Agents Evaluated with Epoxy Resins in ESTC Formulations

Diamino Diphenyl Sulfone  
Modified Aromatic Amines  
Cycloaliphatic Amines  
Diethyltoluene Diamine  
Imidazoles  
Polyglycol Diamine  
Boron Trifluoride/Amine Complexes  
Dicyandiamide  
Dicarboxylic Anhydrides

---

TABLE IV

Inorganic Materials Evaluated as Fillers in ESTC

Beta-Eucryptite  
Synthetic Beta Eucryptite  
Fused Silica  
Schott Glass  
Sub-Micron Silica  
Potassium Titanate Whiskers  
E Glass, Chopped Strand  
Carbon Fiber, Chopped Strand

Lewis acids such as boron trifluoride complexes can be used, but tend to be brittle unless they are toughened. Aromatic amines containing methylene dianiline were not considered because of health questions.

An epoxy curing agent possessing a good overall balance of reactivity, cured properties, and handling as an ESTC is a diamine based on toluene (Figure 13). It is slower reacting than most aromatic diamine curing agents, thus allowing time for mixing in large quantities of filler, yet will cure sufficiently overnight at 80°C to allow removal from the pattern without distortion. Most of the ESTC development was done with compositions using this curing agent. Its primary drawback is that the T<sub>g</sub> that can be developed with this amine is around 150°C. Although it maintains hardness at temperatures up to 180°C, a higher T<sub>g</sub> is still desirable.

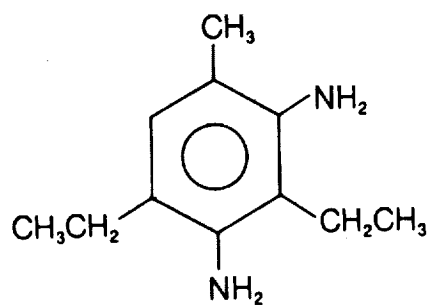
Late in the program, a new resin became available. This resin is based on cyanate ester (CE) technology. Figure 14 shows a representation of the CE resin and reaction. This resin can be co-reacted with liquid Bis A epoxy resins to give a cured composition with T<sub>g</sub> of 180-190°C. These CE epoxy systems can be made into an ESTC that handles using the previously developed techniques, and becomes a cured ESTC surface that performs well and retains strength up to at least 175°C.

The inorganic filler used in the ESTC is the primary determinant of CTE and thermal conductivity, and a major factor in flow behavior and shrinkage. In order to achieve very low CTE, the highest possible loading of filler was desired, and for most compositions, this was 80±5 percent (weight). The fillers used in this work are listed in Table 4. In order for the ESTC to have proper flow behavior, the majority of the filler must be in the form of roughly spherical particles smaller than 75 microns. Fused silica was used for most of the experimental work because it is readily available and inexpensive. Beta-Eucryptite has one of the few known negative CTE values. As such, it offers the best opportunity as a filler in an ESTC to achieve the lowest possible CTE. At least two companies in the U.S. are working on development of a Synthetic Beta Eucryptite (SBE). Twenty-one samples of SBE were evaluated in ESTC formulations. This included samples from both sources, various particle sizes, and different surface treatments. ESTC compositions with inorganic portions ranging from 72 percent to 83.5 percent were achieved with these samples.

In an attempt to improve the tensile strength of the ESTC, glass or carbon fibers were added in concentrations up to 15 percent. When the chopped fibers were added so as to retain most of their original length, the resulting mix became unhandlable as an ESTC. It was found that when these fibers were added early in the mixing process and then broken down in-situ, the tensile strength was increased by 40 percent and the fibers also acted to prevent the ESTC from slumping from vertical surfaces. The typical fiber length after this processing is less than 1mm. An 8 percent addition of glass fiber provides optimum benefit. When an equivalent volume percentage of carbon fiber was used, there was no measurable improvement in CTE, and no advantage in using carbon fibers.

A number of additives were evaluated in ESTC formulations in order to achieve desired effects. A silicone anti-foam is used at 0.0025 percent and helps in obtaining better air removal during vacuum mixing. The use of silanes as filler treatment for coupling is beneficial. Treatment of the fused silica filler with 0.25 percent epoxy silane allowed the filler content to be increased 2-3 percent. Addition of liquid silanes to the formulation did not provide any improvement, and in fact, led to increased porosity of the sheet. A number of other additives such as titanates, zirconates, and organic wetting agents did not provide improvements in either filler loading, processing, or strength.

## DIETHYLTOLUENEDIAMINE



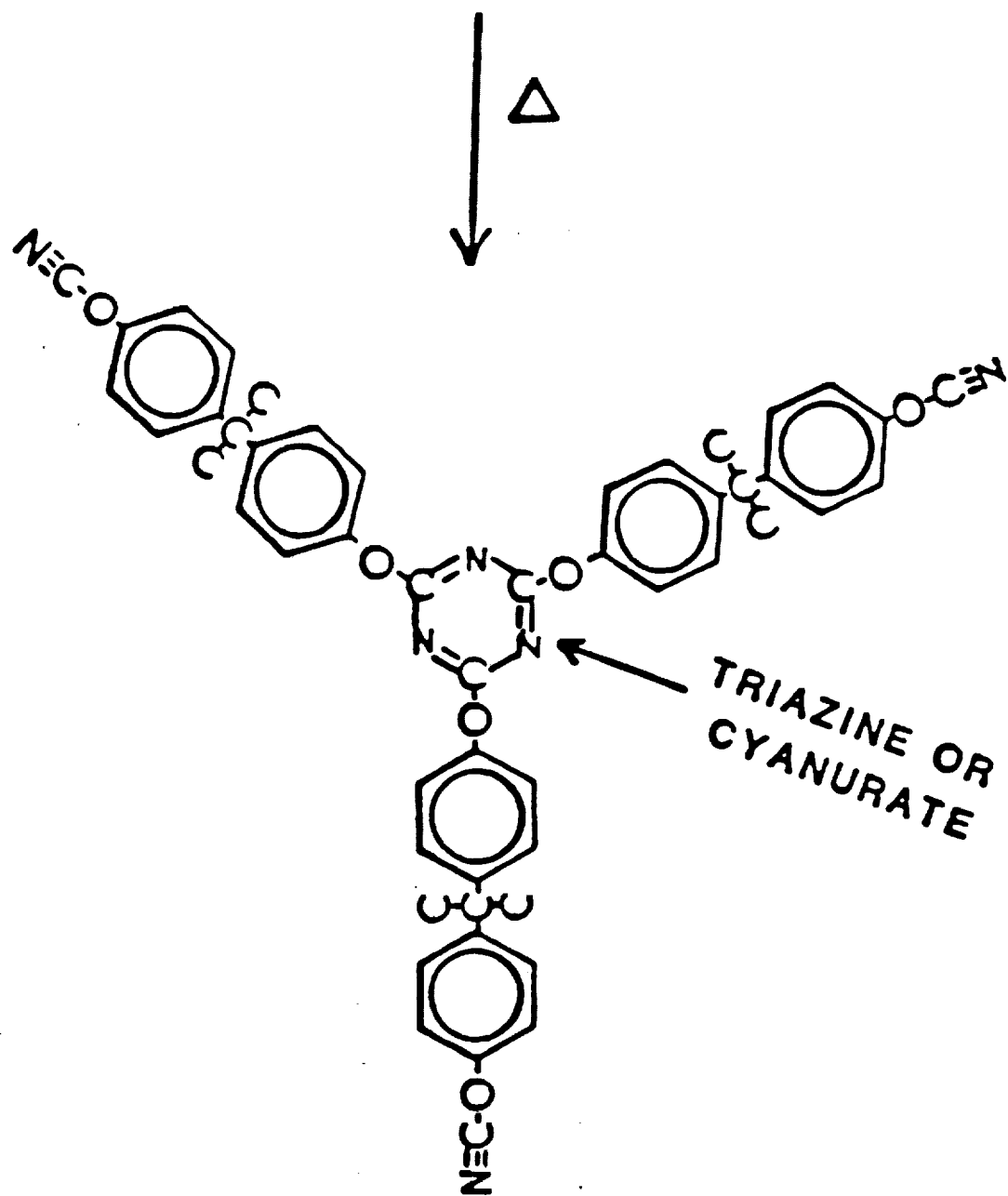
(Major isomer)

Figure 13 -- Diamine Curing Agent for ESTC

## TRIMERIZATION



BISPHENOL A DICYANATE MONOMER



PREPOLYMER  $\xrightarrow{\Delta}$  CURED THERMOSET PLASTIC

Figure 14 -- Cyanate Ester Resin and Reaction Product

An attempt was made to incorporate release agents into the formulation in order to prevent adhesion of the ESTC to the pattern. Several materials that are known to be internal release agents for epoxy were added to an ESTC. None of these additives gave release from the different pattern materials. The quantity of additive was limited to 1 percent to minimize negative effects on the ESTC. It was decided not to add any release since none was found that worked with all normal pattern materials.

An uncured sheet of early ESTC required careful handling to prevent tearing during application and breakage when the sheet was cold. Original formulations contained less than 5 percent of small (5-10 microns) potassium titanate fibers. Further study showed that these fibers did not improve strength or reduce CTE so their use was discontinued. Another way to improve sheet handling strength could be to use a fabric backing such as a thin woven veil of carbon or glass fibers. This works well for improving handling, but when such a backed ESTC was used over patterns with vertical sections, the fabric prevents the ESTC from conforming to some of the pattern surface. Addition of fibrous glass or carbon as described above improved ESTC strength both in the cured and uncured states, and gave easier handling of the sheets.

The effect of ESTC sheet thickness was investigated. Early in the program, interest had been expressed in a thin (2-3mm) sheet of ESTC. ESTC can be formed to that thickness but is very difficult to handle without tearing. In addition, it is so pliable at that thickness and conforms so easily to the pattern that it is much more difficult for air to escape. Such a thin sheet would have to be supplied on a carrier fabric and would be limited to use on relatively simple shapes. ESTC sheets over 10mm thick were also difficult to handle. The optimum ESTC sheet thickness is 5-8mm.

#### 5.0 ESTC Manufacturing Process

In order to achieve the desired final properties and handling characteristics for the ESTC, it is necessary to add the highest possible content of inorganic filler to the composition. The best equipment for this is a high torque mixer such as a Sigma blade mixer. Mixers of three different working capacities were used in this study. One that will mix 500-1000 grams for initial experiments; one that will mix 3-4 kilograms, which will give two (2) sheets of ESTC, and a production size mixer for batches 150-250 kilograms in size. The standard procedure for compounding ESTC is to add most of the particulate filler and the fiber to the mixer, and then mix until the fibers are broken down. The mixer is heated to about 60°C and the pigments, resin, and curing agent mix is added and mixed until uniform. The remainder of the filler is then added and mixed under vacuum until the mass is homogeneous. The mix is then removed and pressed into sheets of the desired size. The time required to thoroughly mix an ESTC is 2-4 hours, depending upon the specific formulation. In evaluating a new composition, a multi-step addition of filler is used to determine the maximum workable loading.

During the evolution of this manufacturing process, several problems were encountered that required changes in procedure. The first ESTC formulation was based on an epoxy-amine chemistry used in many current composites. The epoxy resin is high in viscosity and the amine is a solid so that mixing at over 90°C was required. Attempts to scale up to larger batches resulted in uncontrolled reactions, and after several unsuccessful attempts to modify the chemistry, this composition was abandoned. Initial attempts to mix glass fibers and the mineral fillers resulted

in agglomerates of small glass fibers that did not completely disperse with further mixing. These agglomerates are similar to those found in typical commercial milled glass fibers. By holding mixer temperature close to room temperature and being careful not to overmix, it is possible to properly break down fibers and disperse these in the particulate filler.

The initial method for forming ESTC into sheets was to use a hydraulic press and squeeze the ESTC from the mixer to the desired thickness between two plates. A major study was undertaken to determine if a sheet could be extruded directly to size. The production mixer is designed with two mixing blades, plus a center (bottom) screw that can be run to extrude mixed material. A heated die was built for the extruder. The die was designed to produce a finished sheet 0.635cm thick and 60cm wide. The mixer was not successful in extruding this highly filled material. A consultant was called in and suggested that a separate extruder would be needed for this heavy mix. Studies were then run on calendering equipment. Sheets could be formed after 2 or 3 passes on the calender. There was some tendency for the ESTC to stick to the rolls, but the most significant problem is that the sheets were not dimensionally uniform.

It was decided that an excessive amount of time and money would need to be spent in developing an extruder or calender sheet production system, and that improving the process of pressing of the sheets in molds offers the best short-term solution. The process is slow, but it does allow quite a bit of flexibility in selecting sheet size. Later, this process can be made more efficient with minimum effort.

#### 6.0 ESTC Compositions and Properties

Two formulations have been identified that can be used to make a variety of ESTC compositions, depending on the specific properties needed:

- A. High performance -- Table V shows a typical formulation for ESTC based on a cyanate ester/epoxy resin system. This ESTC is designed to make tools that can be used at temperatures up to at least 180°C. The procedures described earlier are used to form the tool. A precure temperature of 85-90°C overnite is suggested to allow removal from the pattern and then backing. Final cure is 2 hours at 150°C, plus 4 hours at 180°C. If a higher operating temperature is anticipated, then an additional postcure of one (1) hour at 220°C is recommended. Cured physical properties of an ESTC made using fused silica filler are shown in Table VI. Figure 17 shows the hot hardness of the cured ESTC at various temperatures.

The CTE of the ESTC is a function of the mineral filler identity and concentration. Figure 15 shows CTE values for this ESTC filled with fused silica, and Figure 16 with SBE at a total inorganic content of 80 percent. These values were determined using Thermo Mechanical Analysis.

This ESTC is easy to use in forming tools. Very good pattern reproduction is achieved and there is little tendency to trap air. Compression molds made with this ESTC functioned well and there is no evidence of chemical or other attack on the mold surface. The ESTC sheets can be manufactured with minimal problems and exhibit greater than 6 months shelf life when stored at -18°C. Working life at room temperature is over 5 days.

- B. General use -- Table VII shows a typical formulation for an ESTC to make tools useful at moderate temperatures up to about 160°C. This composition is more reactive than the high performance ESTC described above, and thus requires more care during manufacture. Standard procedures are



TABLE V

Typical ESTC Formulation Based on CE Resin

CE Monomer . . . . .	5.0%
CE Prepolymer. . . . .	5.0
Diglycidyl Bis A Epoxy . . . . .	9.5
Fused Silica, Silane Treated . . . . .	71.0
E Glass. . . . .	8.0
Pigment. . . . .	0.5
Catalyst Mix . . . . .	<1.0
	<u>100.0%</u>

TABLE VI

Typical Cured Physical Properties of ESTC Made Using Formulation of Table V

Specific Gravity . . . . .	1.75
Flexural Strength, MPa . . . . .	92
Flexural Modulus, GPa. . . . .	7.9
Tensile Strength, MPa. . . . .	68
Compression Strength, MPa. . . . .	185
Coefficient of Thermal Expansion, -30°C to +30°C, mm/mm/°C, Fused Silica Filler. . . . .	$9.6 \times 10^{-6}$

Sample: 115-66-X2

Size: 6.124 MM 5 CM LOAD

Rate: 05 C/MIN 20 CC/MIN N2

Program: TMA Analysis V2.0

## TMA

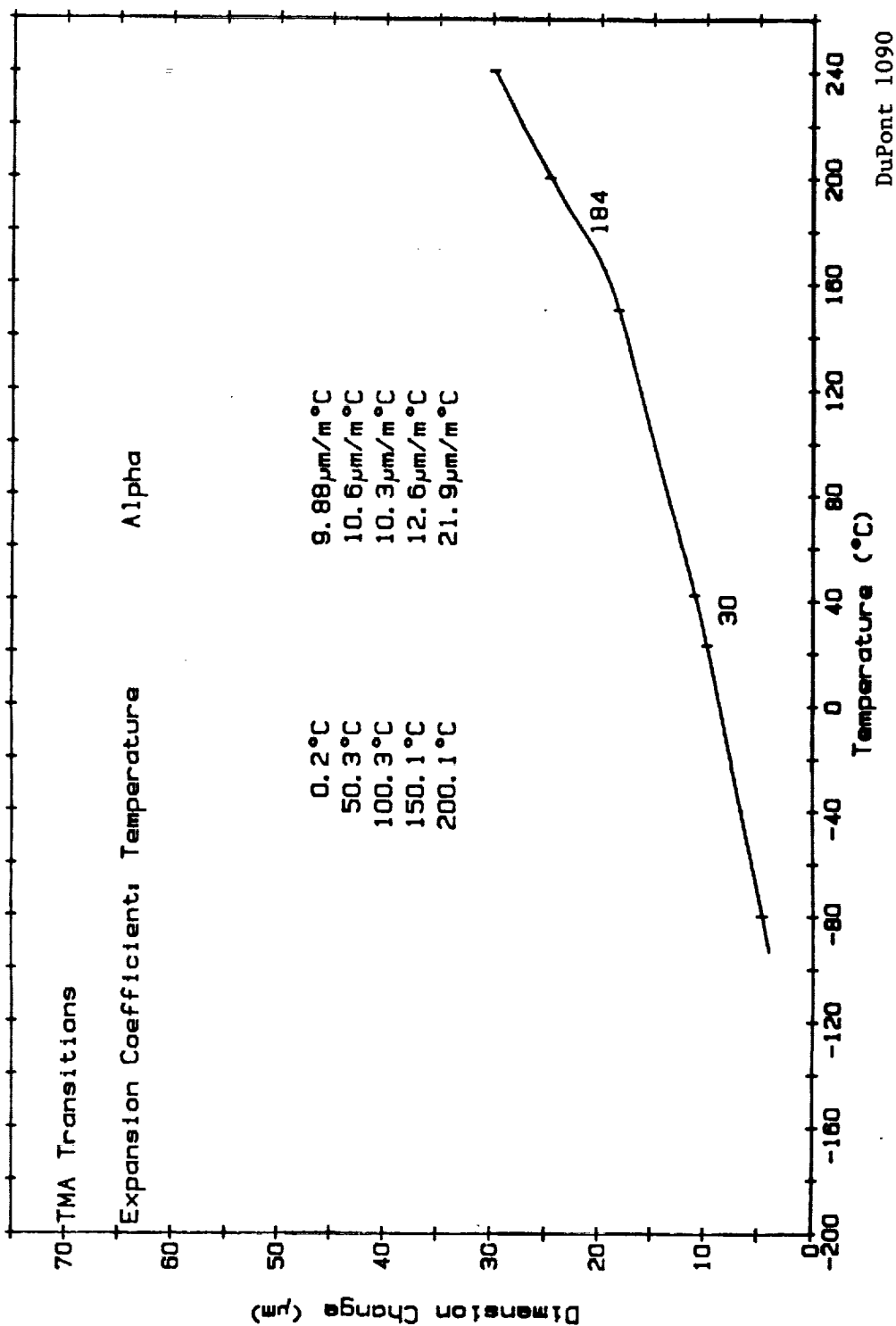


Figure 16 -- Coefficient of Thermal Expansion; CE Resin with Fused Silica Filler Version of ESTC

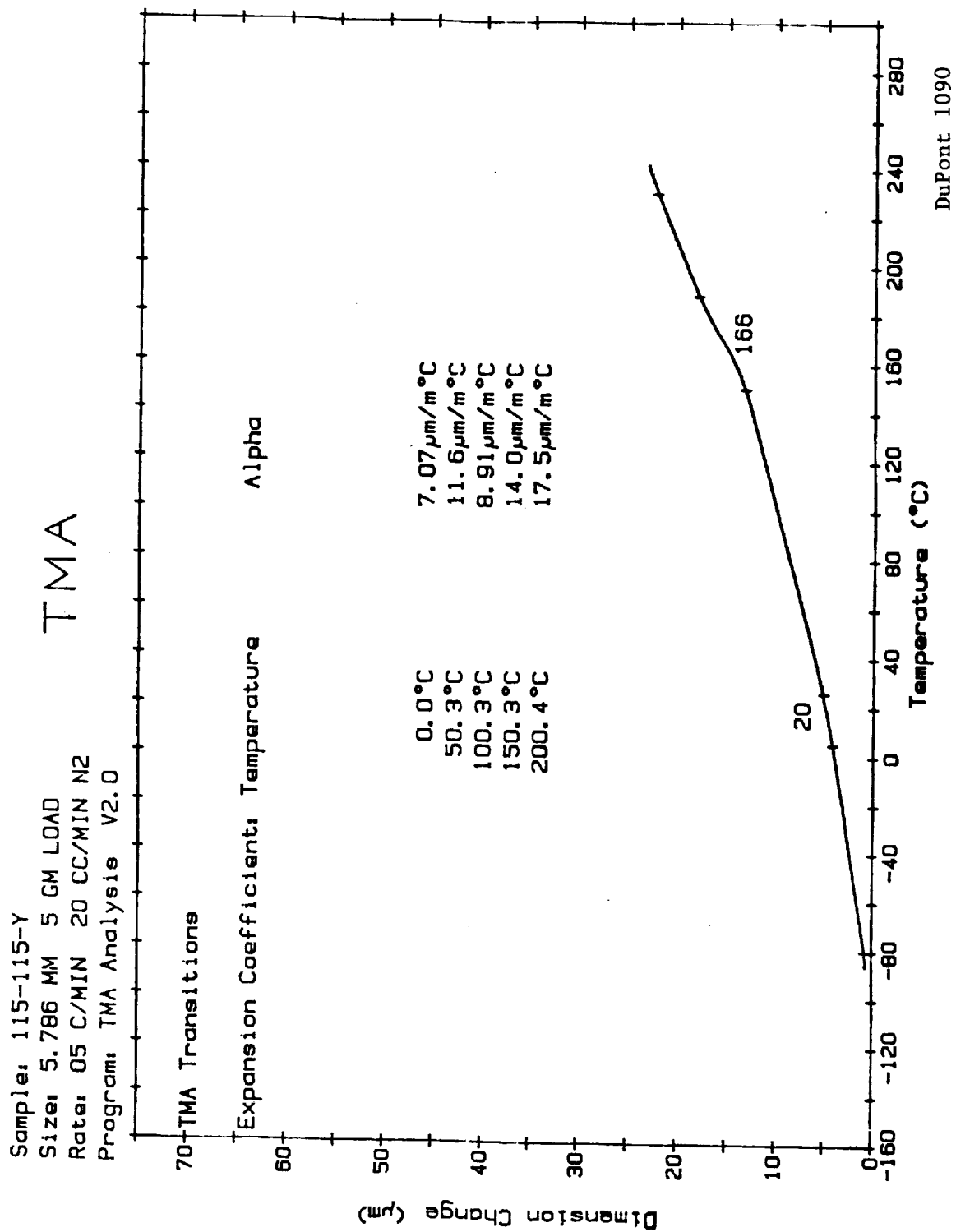


Figure 16 -- Coefficient of Thermal Expansion; CE Resin with SBE Filler Version of ESTC

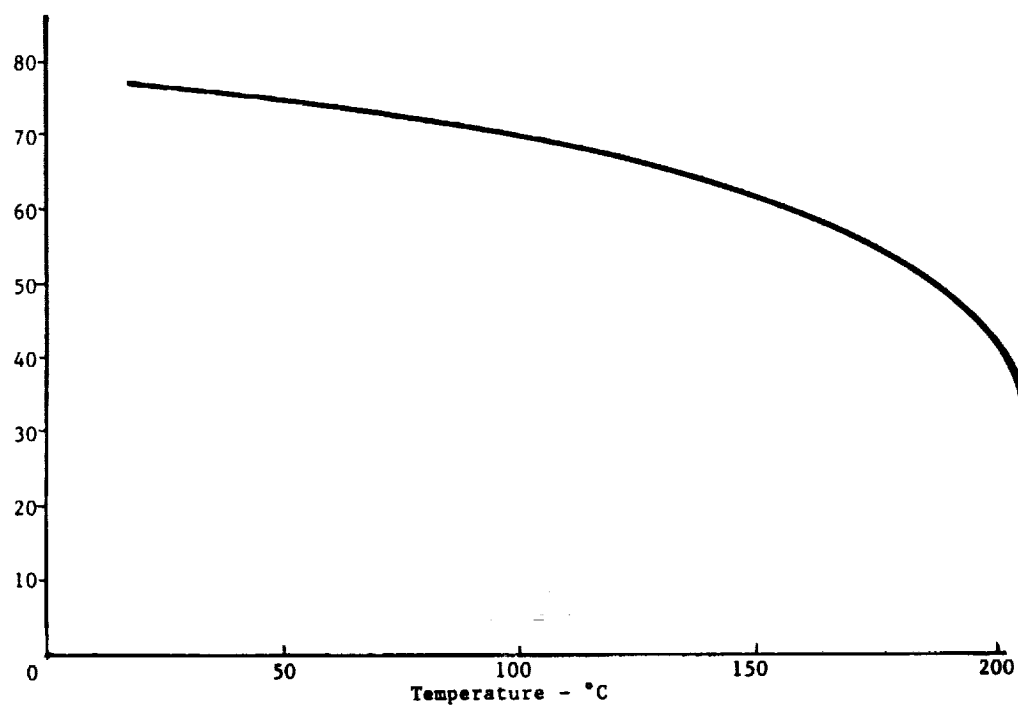


Figure 17 -- Hot Hardness for CE ESTC; Barcol Hardness of ESTC Measured at Temperature.

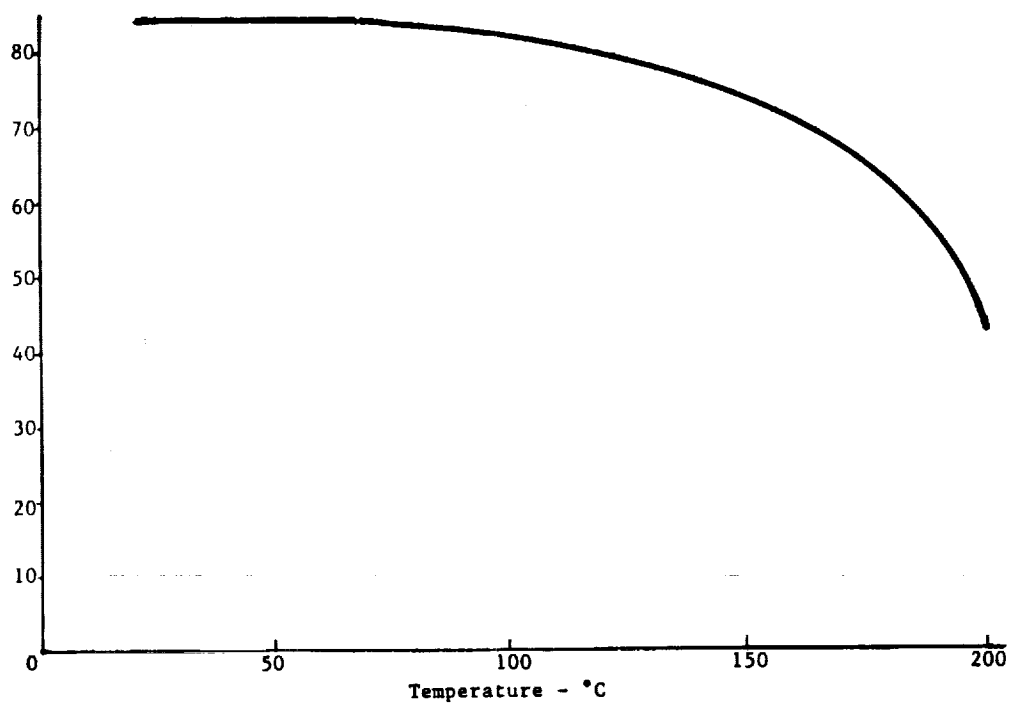


Figure 18 -- Hot Hardness of Epoxy/Amine ESTC; Barcol Hardness Measured at Temperature

Sample: 104-82-Z2  
 Size: 6.683 MM 5 GM LOAD  
 Rate: 5 C/MIN 20 CC/MIN N2  
 Program: TMA Analysis V2.0

# TMA

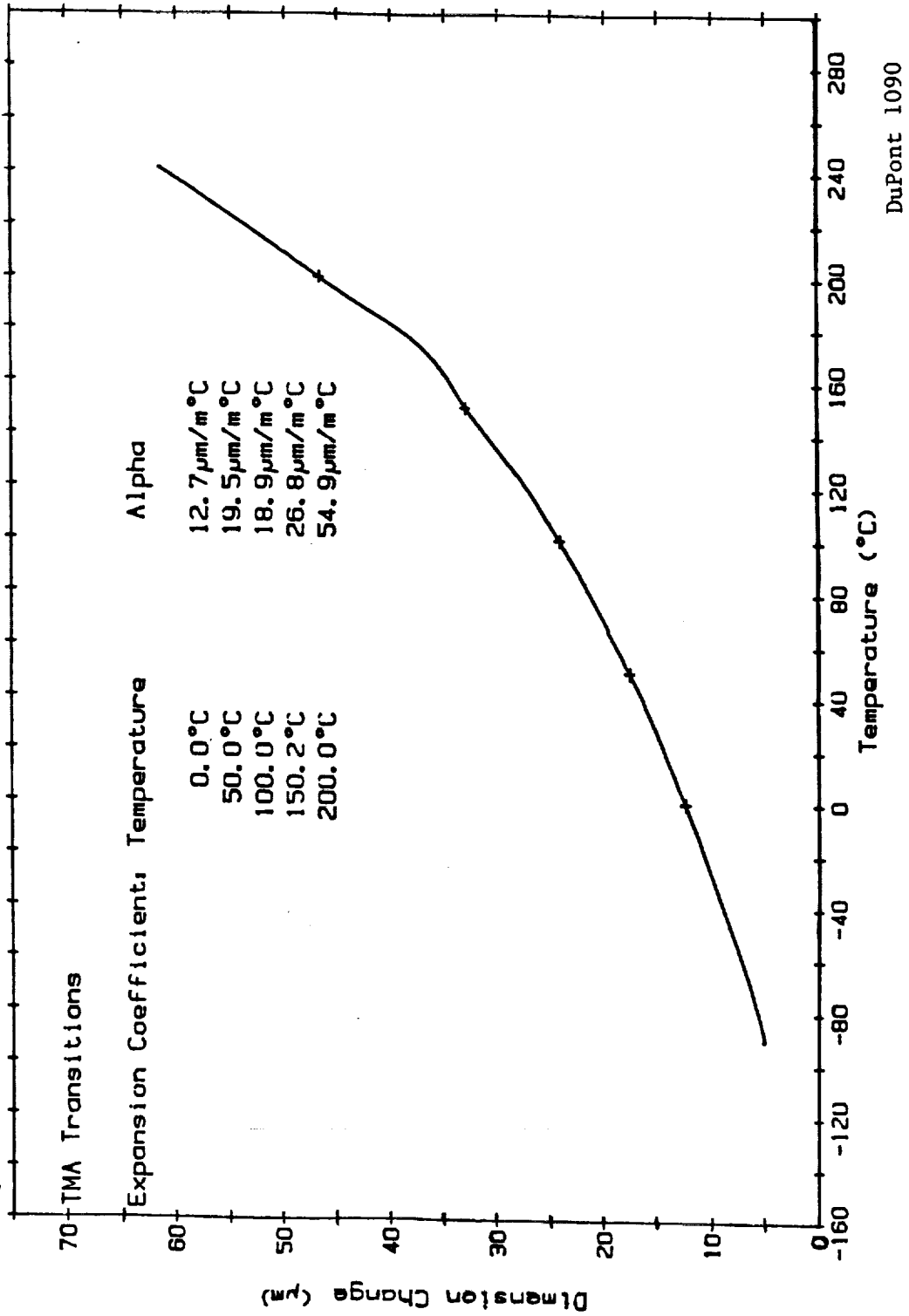


Figure 19 -- Coefficient of Thermal Expansion; Epoxy/Amine with Fused Silica Filler Version of ESTC

TABLE VII

Typical ESTC Formulation Based on Epoxy/Amine

Diglycidyl BisA Epoxy . . . . .	15.2%
Diethyl Toluene Diamine . . . . .	3.8
Fused Silica, Silane Treated. . . . .	72.5
Pigment . . . . .	0.5
E Glass . . . . .	8.0

TABLE VIII

Typical Properties of ESTC (Epoxy/Amine)

Specific Gravity . . . . .	1.88
Flexural Strength, MPa . . . . .	88
Flexural Modulus, GPa. . . . .	13
Compressive Strength, MPa. . . . .	190
Tensile Strength, MPa. . . . .	50
Coefficient of Thermal Expansion, -30°C to +30°C, mm/mm/°C . . . .	$13 \times 10^{-6}$

used to form a tool. Precure of overnite at 75°C is followed by 4 hours at 150°C for full cure. The cured physical properties of this ESTC made with fused silica filler are shown in Table VIII. Figure 18 shows the hot hardness of the cured ESTC at various temperatures, and Figure 19 shows CTE values.

Most of the development work in the program has used ESTC similar to this. A number of tools have been made and used to fabricate parts using a variety of processes. Shelf life of the material is 6 months at -18°C, and working time at room temperature is 2 days.

- C. Room temperature cure -- Many of the pattern materials that are used in tool making are temperature sensitive. Wood and plaster can be used at temperatures up to 80-90°C, but extreme care must be used and the patterns must be well sealed to prevent water escape into the tool. Foam is being widely used and is not stable much above room temperature. An ESTC that is applied and will harden at room temperature could be useful in those situations. Attempts to use epoxy curing agents that can cure at room temperature to make ESTC were unsuccessful. These systems are so reactive that it was impossible to make a consistent product with the required ESTC handling properties.

The "general use" ESTC described above will harden at room temperature, if enough time is allowed. After 5-7 days at approximately 25°C, the ESTC is sufficiently cured to retain its shape on removal from the pattern. It is then desirable to back the ESTC immediately and then provide controlled heating to complete the cure.

- D. Thin ESTC -- Periodic interest has been expressed in ESTC that is about 2mm thick for use like a gel coat. ESTC sheets can be made at that thickness, but, as described earlier, the sheet is very fragile and difficult to handle. Because it is so pliable, it conforms easily to the pattern and entrapped air is difficult to remove. This is not a practical use for ESTC.
- E. Other variations -- ESTC materials are not limited to the specific compositions described above. Changes in resins, curing agents, catalysts, fillers, and even polymer types are all theoretically possible in order to modify some characteristic of the material. In practice, there are a limited number of modifications that have practical value. One example is the use of particulate aluminum metal as the filler in order to achieve better thermal conductivity. In this case, the CTE would increase several fold, and the backing for the tool must be constructed to take this difference into account. Carbon particles might also be used as the filler in order to achieve better heat conductivity while retaining moderately low CTE, but this was not tried experimentally. Multiple sheets of ESTC can be stacked and will fuse together during cure.

#### 7.0 Markets

During the final half of this program, the concept of ESTC and the material were introduced to a number of potential users. Some of these contacts resulted in evaluations which are described earlier; some resulted in expressions of future interest; and some resulted in no interest. The majority of these contacts were associated with the aerospace or automotive markets. In the automotive-oriented tooling shops, the interest in an ESTC is mixed. Many of the patterns now used

are of foam or similar temperature sensitive materials, and any heating requirement is a problem. There is little interest in low CTE. Probably the greatest potential problem is a reluctance to try something requiring new techniques, particularly until the use has been proven and well established. There are a number of tools where use of ESTC would not be technically feasible because of the design of the particular part. Fortunately, there are some tooling shops interested in looking at new materials. It may be necessary to adjust the formulation of the ESTC for this market, but there is interest for prototype tools, particularly if they can be adapted for injection molding tools.

An ESTC can meet many of the needs for tooling for high performance composites for aerospace applications. The goal of an ESTC with a CTE matching that of carbon fiber prepreps are not fully met. Addition of 80 percent (weight) of the particulate filler with the most negative CTE that is commercially available (SBE), results in an ESTC having a CTE approximately twice as high as that of a typical carbon fiber/epoxy prepreg. The low CTE of a carbon fiber prepreg is achieved when the expansion is measured in the direction of the fibers and is controlled by the CTE of these continuous fibers. Based on these studies, it is unlikely that any known organic resin matrix containing primarily particulate inorganic filler can achieve a CTE matching that of the typical carbon fiber prepreg. The use of ESTC with its relatively low CTE to fabricate tools will still require compensation for differences in CTE between pattern, tool, and finished part as is now done, but it should be easier than when using conventional tooling materials.

The reduction in CTE achieved using SBE filler instead of fused silica (Figures 15 and 16) may not be enough to justify the higher cost of the SBE. The projected price of SBE in moderate quantities is around \$35 per kilogram, compared with fused silica at less than \$1.50 per kilogram. This results in a finished ESTC cost over 5 times as high with SBE as with fused silica. For most uses, the slightly higher CTE of a fused silica filled ESTC will be acceptable in light of the better economics.

Reductions in CTE can be achieved by backing the ESTC with several layers of carbon fiber fabric. The CTE of this combination will come closer to the CTE of a carbon fiber prepreg.

The ESTC based on use of CE resins exhibits a  $T_g$  greater than  $180^\circ\text{C}$ , and maintains good hardness and integrity at that temperature. Depending upon exact conditions involved, it should also perform satisfactorily for some tooling applications at  $200^\circ\text{C}$  or more. This version of ESTC is ready for outside evaluation.

A market survey<sup>2</sup> of ESTC potential was conducted by two students at a local college. They interviewed a number of potential ESTC users and concluded that a combination of user education and promotion will be needed to establish use of ESTC.

#### Conclusions:

1. ESTC can be manufactured and practical tools for composites fabrication can be made using ESTC.
2. The primary use for such tools will be for small production runs and prototype studies.
3. ESTC must be used as part of a tooling system. A backing for the ESTC that is thermally compatible is particularly important.

<sup>2</sup>Marketing Research for Quantum Composites, Inc. by Tony P. Dragotto and Donald J. Maday, Small Business Institute, Northwood Institute, Midland, MI



4. It will require considerable time and effort to develop broad usage of ESTC because of reluctance to change from established procedures and the need to demonstrate successful use before some organizations will consider its use.
5. A summary of the major advantages and disadvantages of ESTC, as shown by the development efforts, are noted below:

Advantages:

1. Fast -- Some tools can be made in less than 2 days
2. Low cost
3. Very good properties at elevated temperature
4. No problems of gel coat cracking

Disadvantages:

1. Requires different use techniques
2. Requires a heat cure which some tool shops are not equipped to do
3. CTE is not as low as carbon fiber prepregs
4. Thin sections are not strong enough for high pressure use without supplemental support
5. Thermal conductivity is low

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16. Abstract  <p>An Extruded Sheet Tooling Compound (ESTC) has been developed for use in quickly building low cost molds for fabricating composites. The ESTC is a very highly mineral-filled resin system formed into a 6mm thick sheet. The sheet is laid on the pattern, vacuum (bag) is applied to remove air from the pattern surface, and the assembly is heat cured. The formed ESTC is then backed and/or framed and is ready for use.</p> <p>The cured ESTC exhibits low Coefficient of Thermal Expansion and maintains strength at temperatures of 180-200°C. Tools have been made and used successfully for: Compression molding of high strength epoxy sheet molding compound, stamping of aluminum, Resin Transfer Molding of polyester, and Liquid Resin Molding of polyester.</p> <p>Several variations of ESTC can be made for specific requirements. Higher thermal conductivity can be achieved by using and aluminum particle filler. Room temperature gel is possible to allow use of foam patterns.</p>			
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